Growth of Si on different GaAs surfaces: A comparative study

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We studied the chemical bonding at the interface between Si and GaAs by synchrotron radiation photoelectron spectroscopy. Thin Si films were deposited at 450 °C or 500 °C on different GaAs substrates: the As-rich GaAs(100) and GaAs(111)B surfaces as well as the Ga-rich GaAs(100) and GaAs(111)A surfaces. In this paper we compare the properties of these four interfaces. On As-rich GaAs the Si bonds solely to As. No Ga-Si bonds are formed. The Si atoms occupy the equivalent of next-layer Ga sites. Neither As nor Ga segregation to the surface of the Si film is observed. On the Ga-rich GaAs(100)-(4×2) and GaAs(111)A surfaces Ga-Si bonds are formed at the interface. Arsenic segregates to the surface of the Si film, leaving As vacancies behind at the interface. While these results can be understood in terms of simple models, the behavior of the As-rich GaAs(111)B surface is more complicated. We discuss this surface in detail.

I. INTRODUCTION

The growth of Si on GaAs has recently attracted attention for technological applications. Defect-free epitaxy is not so straightforward because the lattice mismatch between Si and GaAs is 4%. Since Si can be used as a dopant in GaAs, δ doping with a submonolayer of Si was studied in detail.[1] The successful growth of Si-GaAs(100) superlattices was reported in Refs. 2 and 3. Furthermore, the valence-band offset between AlAs and GaAs can be tuned by nearly 1 eV using a Si intralayer.[4,5] A Si interface layer can also be used to modify the character of the Schottky barrier between metals and GaAs.[6–10] Considering the potential of thin Si layers on GaAs for high precision doping or band-gap engineering it is surprising that only a few papers deal with the structural and electronic properties of these films.[11–14]

We deposited Si on As-rich GaAs(100) and GaAs(111)B as well as on Ga-rich GaAs(100) and GaAs(111)A. Several growth parameters were varied to gain a deeper understanding of the properties of thin Si films on GaAs. Some structural results have already been published in Ref. 15. In this paper we report the results of our photoelectron spectroscopy experiments. Very surface sensitive synchrotron radiation photoelectron spectroscopy was employed to clarify the chemical bonding at the interface between Si and GaAs.

II. EXPERIMENTAL DETAILS

Sample preparation and experiments were performed at beamline BL-1A of the Photon Factory in the National Laboratory for High Energy Physics in Tsukuba, Japan. The photon energy for the synchrotron radiation photoelectron spectroscopy (SRPES) experiments was adjusted using a grating-crystal monochromator with a 1200-mm^{-1} grating. For our experiments we used a photon energy of 130 eV. The accuracy and reproducibility of the monochromator were checked by directly measuring the Fermi edge and the $4f$ peak of a reference gold sample. It was found that photon energies were exact to within ±0.1 eV. Details of the beamline are described elsewhere.[16,17]

The experiments were carried out in ultrahigh vacuum (UHV). The experimental chamber consisted of an analysis chamber and a chamber for molecular beam epitaxy (MBE). These were connected by a transfer chamber with a load lock for fast sample exchange. The analysis chamber was equipped with an entrance port for the synchrotron radiation, a conventional x-ray source (Al $K\alpha$ and Mg $K\alpha$) for x-ray photoelectron spectroscopy (XPS), and an angle integrating hemispherical photoelectron energy analyzer. Sample preparation was done in the MBE chamber.

400-μm-thick Si-doped n-type GaAs substrate wafers were used for these investigations. The carrier concentration was 1×10^{18} cm^{-3}, which resulted in a resistivity of $\rho\approx3\times10^{-3}$ Ω cm. The wafer surfaces used for these experiments were mirrorlike polished and oriented with an accuracy of ±0.50°. The etch pit density of the wafers was specified to be less than 1×10^{4} cm^{-2}.

The GaAs wafers were dipped in a commercial alkaline-based etchant for 5 min. Following this, the sample was rinsed in purified water and dried with N_2 gas. The etched GaAs wafers were then attached to a Mo sample holder with In solder and placed in the vacuum chamber.

The GaAs substrate was then heated in an As overpressure for about 10 min at 600 °C to desorb the surface oxides. For different sample orientations and desired surface reconstructions, the subsequent procedures were used: (i) GaAs(100)-(2×4): At 550 °C a GaAs buffer layer was grown. The surface of this buffer layer was well ordered and showed a (2×4) reconstruction. (ii) GaAs(100)-c(8×2): After a GaAs(100)-(2×4) surface was obtained as described in (i), the As K-cell shutter was closed. After a bright c(8×2) superstructure was obtained, the Ga K-cell shutter was also closed. (iii) GaAs(111)A: After the native oxide was removed, a sharp (2×2) reconstruction was obtained, so we did not grow a buffer layer on this surface. (iv) GaAs(111)B. After the native oxide was removed, a high-quality GaAs buffer layer was grown at 550 °C. The buffer layer surface after growth showed a sharp (1×1) reflection high-energy electron diffraction (RHEED) pattern at 550 °C. After cooling this sample to 500 °C or below, a bright (2×2) was ob-

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tained, in agreement with the results of Woolf, Westwood, and Williams.[18]

Three K cells in the MBE chamber were used for As, Ga, and Si evaporation. The parameters for GaAs MBE were as follows: As_4 beam flux 3×10^{-6} torr and Ga beam flux 4.5×10^{-8} torr, which corresponds to a growth rate of 450 Å of GaAs per hour. The flux values were determined with an ion gauge positioned at the sample location. The Si K cell was operated at 1350 °C. The Si growth rate was determined from the attenuation of the substrate core-level photoemission to be 90 Å/h. The only contamination on the surface of the Si film was a small trace of Se (less than 5%). For the (100) orientation, 1 ML of Si corresponds to 6.78×10^{14} atoms cm^{-2}, while for the (111) orientation, 1 double layer (DL) of Si corresponds to 15.6×10^{14} atoms cm^{-2}. This is the surface atomic density of bulk Si. For a pseudomorphic film the real density is slightly different, but the deviation is within the uncertainty of our K-cell calibration.

III. RESULTS

A. Band bending

It is well known that the Fermi energy of GaAs(100) is pinned near the midgap.[19,20] This pinning is caused by surface states in the gap and is the reason for band bending near the surface of the semiconductor. We used XPS to measure the band bending in our samples. The sampling depth of XPS is approximately $3\lambda \sin\theta \approx 50$ Å, where λ is the mean free path for the photoelectrons ($\lambda\approx25$ Å) and θ is the collection angle ($\theta=45°$ in our setup). For substrates with a carrier concentration of 1×10^{18} cm^{-3}, as used in our experiments, the width of the depletion layer can be estimated to be around 400–500 Å. So the sampling depth of XPS is small enough to measure the band bending, but large enough not to be affected by peak shifts due to surface chemical bonding.

We measured the position of both the Ga $3d$ and the As $3d$ peaks. While the distance between these two peaks was constant in all our measurements, their binding energies (given relative to the Fermi energy) changed when Si was deposited on the GaAs. These changes will be discussed later. The photovoltaic effect discussed in Ref. 21 can be neglected in our measurements, because we made our measurements at room temperature on highly doped GaAs.

The Ga $3d$ peak for the uncovered GaAs substrates was measured at a binding energy of 19.5 eV. The distance between the Ga $3d$ peak and the valence-band maximum (VBM) is, according to the literature, 18.8 eV.[4,19,22] So at the surface of the GaAs samples the Fermi energy is located 0.7 eV above the VBM. Almost the same value was measured for all samples, i.e., for As-rich and Ga-rich GaAs (100) and (111) surfaces. It corresponds to the midgap position and is in agreement with the results published in Ref. 20 for n-type GaAs(100).

After deposition of Si at 450 °C or 500 °C the position of the Ga $3d$ peak shifted to higher binding energies. This is shown in Fig. 1. The shift was 0.3–0.4 eV after deposition of 4 ML (or 2 DL) of Si. We might first attempt to explain this shift with a relaxation of the band bending, but a more careful analysis is necessary. We deposited the Si without intentional doping, or, in other words, without As or Ga flux. According to Silberman, Lyon, and Woodall the deposition

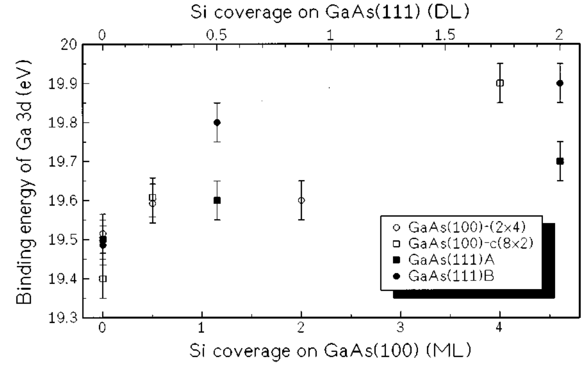

FIG. 1. Binding energy (with respect to the Fermi energy) of the XPS Ga $3d$ peak for different surfaces as a function of Si coverage. We measured the band bending for the As-rich GaAs(100)-(2×4) and GaAs(111)B surfaces as well as for the Ga-rich GaAs(100)-c(8×2) and GaAs(111)A surfaces. The peak positions are given as a function of the number of deposited Si atoms. One double layer (DL) of Si(111) corresponds approximately to two monolayers (ML) of Si(100). The two different x axes reflect the exact ratio between DL and ML.

of an undoped Si layer on GaAs does not remove the Fermi-level pinning.[23] On the other hand, the deposition of a doped Si layer can cause the band bending to relax.[22,24] While Silberman *et al.* deposited the Si in a separate chamber, we deposited it in our III-V MBE chamber, so doping from the As background cannot be excluded and will be discussed now. The Si flux during growth in our chamber was 4×10^{-8} torr. The As background pressure in our chamber with the hot Si K cell can be estimated to be 5×10^{-10} torr, so the As supply at the surface was 1% of the Si supply. Since As is volatile, it is unlikely that all the incoming As atoms were incorporated into the Si film, but a dopant density of about 1×10^{19} cm^{-3} seems possible, especially since the solid solubility of As into bulk Si is reported to be 1×10^{21} cm^{-3}.[19] On the other hand, a doping density of 1×10^{19} cm^{-3} is sufficient to explain the observed relaxation of the band.[24] So we assume that the Si we deposited was unintentionally As doped.

Thus, all the GaAs substrates under investigation had the Fermi level pinned in the midgap, 0.7 eV above the VBM. The deposition of a pseudomorphic layer of n-type Si caused a relaxation of the band bending. However, the results of Silberman, Lyon, and Woodall indicate that the surface states of GaAs, which are responsible for the Fermi-level pinning, are not removed even when a highly ordered epitaxial Si overlayer is grown. But the high charge density in the overlayer compensates for the interface state charge.

B. Photoelectron spectra

1. General remarks

To obtain information about the chemical bonding at the interface and surface of the samples, we performed synchrotron radiation photoelectron spectroscopy. In general, for each of the four substrates used in these experiments, As-rich and Ga-rich GaAs(100) and GaAs(111), three different sets of spectra were measured: one for the clean surface, one after deposition of 0.5 ML or DL of Si, and a third one after deposition of more than 1 ML or DL of Si. Each set of

TABLE I. Summary of chemical shifts in the As 3d and Ga 3d core-level spectra. The values are given with respect to the bulk As-Ga bonding position. A + sign indicates a shift to higher binding energies, while a − sign indicates a shift to lower binding energies.

	As 3d peak
As-As	+0.60 eV±0.10 eV
As-As (Ref. 27)	+0.70 eV
As-Si	−0.49 eV±0.06 eV
	Ga 3d peak
Ga-Ga	−0.85 eV±0.11 eV
Ga-Ga (Ref. 26)	−0.71 eV±0.02 eV
Ga-Si	−0.41 eV±0.06 eV

spectra included a measurement of the As 3d, Ga 3d, and Si 2p peak with a photon energy of 130 eV.

The deposition of Si on GaAs always resulted in Si 2p core-level spectra with a poorly resolved structure. A deconvolution of these peaks was found to be somewhat arbitrary. The problem probably arises from the different bonding partners of the Si, namely, Si, Ga, and As, which should produce distinct core-level shifts. Furthermore, disorder associated with specific sites will lead to broadening. Other authors reported the same problems.[11,22] Since no unequivocal deconvolution was possible for the Si 2p peaks, we will concentrate in this paper on the As 3d and Ga 3d peaks. These peaks were analyzed using very strict parameter conditions. Both peaks were deconvoluted using the following parameters: the $3d_{3/2}$ and $3d_{5/2}$ components were described by Voigt functions. The Gaussian and the Lorentzian functions in the Voigt function had the same half-width (FWHM), and their intensity ratio was described by a parameter m, where $m=1$ for pure Gaussian and $m=0$ for pure Lorentzian. In detail, the parameters were FWHM equal to 0.55 eV±0.05 eV and $m=0.45\pm0.05$ for Ga 3d and FWHM equal to 0.65 eV±0.05 eV and $m=0.75\pm0.05$ for As 3d. The values for the spin-orbit splitting Δ_{so} and the branching ratio B were constant for all the spectra measured. Their values were $\Delta_{so}=0.45$ eV and $B=1.5$ for Ga 3d and $\Delta_{so}=0.69$ eV and $B=1.4$ for As 3d, which agrees perfectly with a high resolution study of GaAs(100)-(4×2).[20]

The assignment of the bulk components in the As 3d and Ga 3d core-level spectra was confirmed by the fact that the distance between the As $3d_{5/2}$ bulk component and the Ga $3d_{5/2}$ bulk component was found to be the same for all samples. The energy separation between these two peaks was $\Delta E=21.82$ eV ±0.06 eV, which agrees well with literature values.[20] The average energy shifts for components with different chemical bonding are summarized in Table I. A + sign indicates a shift to higher binding energies, while a − sign indicates a shift to lower binding energies. These values agree with literature values, where available.

The binding energies of the As 3d and Ga 3d peaks with respect to the Fermi energy were usually 0.1–0.2 eV smaller than the values measured by XPS. This reflects the higher surface sensitivity of SRPES and further supports the band-bending model.

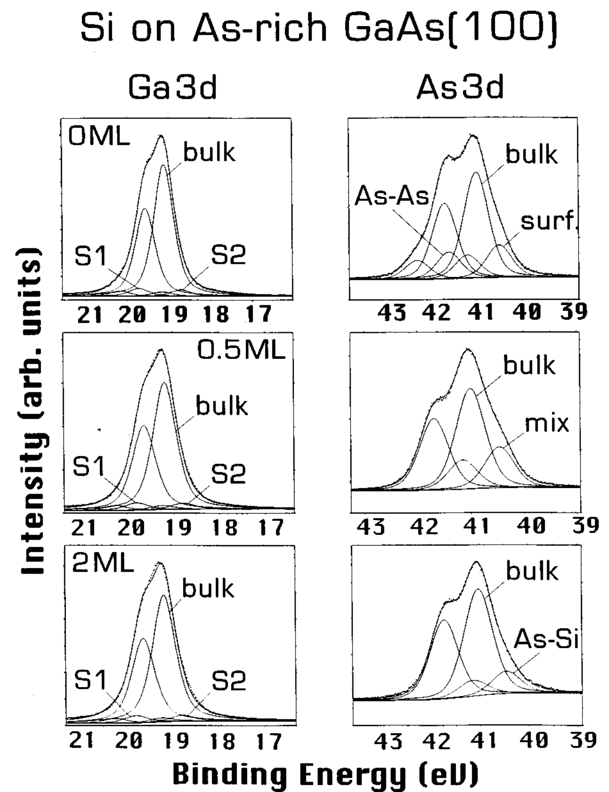

FIG. 2. Surface sensitive Ga 3d and As 3d core-level spectra of As-rich GaAs(100) surfaces as a function of Si overlayer thickness. Ga 3d spectra contain two surface-shifted components at the high ($S1$) and low ($S2$) binding energies from the substrate (bulk). As 3d presents a single surface-shifted component (surf.). Before deposition of Si, As-As bonding produces a spectral component at the high binding energy side of the spectrum, which is attributed to the As dimers of the (2×4) reconstruction. After deposition of Si, As-Si bonds are formed on the surface. For a coverage of 0.5 ML of Si the surf. and the As-Si components coincide as one component (mix). Please note the comment in Ref. 34.

2. As-rich GaAs(100)

The spectra obtained on As-rich GaAs(100) are shown in Fig. 2. The clean surface showed a bright (2×4) reconstruction. After cooling it down to room temperature we measured the photoelectron spectra shown in Fig. 2. After these measurements the sample temperature was increased to 500 °C for the deposition of Si. However, at this point the (2×4) superstructure had disappeared. Nevertheless, the obtained results are characteristic for an As-rich GaAs(100) surface, because in a control experiment we deposited Si under As flux and obtained virtually the same spectra.

The Ga 3d peak of the clean GaAs(100)-(2×4) surface shows a strong bulk component and two surface components, $S1$ and $S2$, at +0.62 and −0.39 eV, respectively. After deposition of 0.5 ML of Si at 500 °C and even after deposition of 2 ML of Si, the Ga 3d peak was virtually unchanged, so we conclude that no Ga-Si bonds were formed. The As 3d peak of the clean GaAs(100)-(2×4) surface has three components: a bulk component, a surface component at −0.47 eV, and a component at +0.60 eV, which we assign with As-As bonds. These values, as well as the deconvolution for the Ga 3d peak, agree quite well with data published in the

literature.[25–27] After deposition of 0.5 ML of Si at 500 °C the As-As bonding component in the As $3d$ peak had disappeared, so we conclude that all As-As bonds were broken by the Si. The substrate component changed slightly its intensity and position. As we will show in Sec. III B 4, the position of the As-Si bonding component is nearly the same as for the As surface component on the GaAs(100)-(2×4) surface. Because the positions of the two peaks are nearly the same, a separation of them was not successful. So we label this component in the As $3d$ peak after deposition of 0.5 ML Si *mix*. After deposition of 2 ML of Si we assume that the surface component in the As $3d$ had disappeared and that the observed component was caused solely by As-Si bonds. The intensity ratio r between the As $3d$ and the Ga $3d$ peaks for the clean surface was $r=0.7$. If we subtract the intensity in the component of adsorbed As from the As $3d$ peak, the ratio becomes $r=0.6$. This ratio was unchanged after deposition of Si. In other words, a segregation of As or Ga to the surface was not observed within the sensitivity of our method. Instead, we always observed stoichiometric GaAs.

3. Ga-rich GaAs(100)-c(8×2)

The spectra measured on the GaAs(100)-$c(8\times2)$ surface are shown in Fig. 3. The Ga $3d$ peak of GaAs(100)-$c(8\times2)$ consists of three components: the main bulk component and two surface components, $S1$ and $S2$, at $+0.39$ and -0.40 eV. This deconvolution is in agreement with the results of Le Lay *et al.* and discussed there in detail.[20] Similar results are also published in Refs. 25 and 26. After deposition of 0.5 ML of Si at 450 °C the $S2$ component has slightly changed its intensity and position. As we will show in Sec. III B 5, the Ga-Si bonding component has nearly the same position as the $S2$ component, so we label this component for 0.5 ML Si as *mix*. On the other hand, the $S1$ component has not changed its position or intensity with respect to the bulk component. After deposition of 4 ML of Si the Ga $3d$ peak has completely changed. The $S1$ component has vanished, and a new component at lower binding energy has appeared, which we assign to Ga-Ga bonds. The As $3d$ peak of the clean GaAs(100)-$c(8\times2)$ surface is composed of a bulk component and a surface component at -0.61 eV. After deposition of 0.5 ML of Si, a slight change in the surface component indicates the creation of As-Si bonds. After deposition of 4 ML of Si, a third component is resolved in the As $3d$ core-level spectrum, which is assigned to As-As bonds. The intensity ratio r between the As $3d$ and the Ga $3d$ peaks changes from stoichiometric $r=0.6$ for the clean surface and after deposition of 0.5 ML of Si to $r=1.5$ after deposition of 4 ML of Si. On the other hand, the intensity ratio of the XPS As $3d$ and the XPS Ga $3d$ peaks is constant. Since XPS is more bulk sensitive than SRPES, we conclude that the bulk composition is still stoichiometric and that the As enrichment occurs solely at the surface.

4. Ga-rich GaAs(111)A-(2×2)

The Ga $3d$ peak of the clean Ga-rich GaAs(111)A-(2×2) surface can be described with just one bulk doublet. The spectra are shown in Fig. 4. To our knowledge no high-resolution photoelectron spectra of the GaAs(111)A surface have been published before. It is somewhat surprising that no

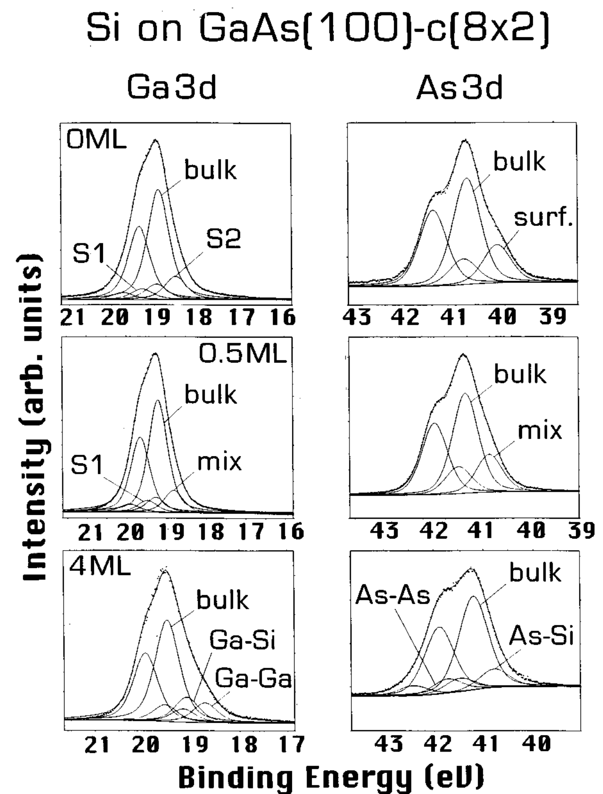

FIG. 3. Surface sensitive Ga $3d$ and As $3d$ core-level spectra of GaAs(100)-$c(8\times2)$ surfaces as a function of Si overlayer thickness. The Ga $3d$ spectrum of the uncovered surface contains two surface-shifted components at the high ($S1$) and low ($S2$) binding energies from the substrate (bulk). After deposition of Si, Ga-Si bonds are formed. For a coverage of 0.5 ML of Si the $S2$ and the Ga-Si components coincide as one component (mix). After deposition of 4 ML Si, Ga-Ga bonds are formed at the interface. As $3d$ presents a single surface-shifted component (surf.). After deposition of Si, As-Si bonds are formed on the surface. For a coverage of 0.5 ML Si the surf. and the As-Si components coincide as one component (mix). After deposition of 4 ML Si, As-As bonds are also formed. Please note the comment in Ref. 34.

surface peak could be detected, but all attempts to deconvolute the peak into two doublets failed. After deposition of 0.5 DL Si at 450 °C a second doublet was clearly resolved in the Ga $3d$ core-level spectrum. This second component was assigned to Ga-Si bonds. Since the situation is clearer for the GaAs(111)B surface, this peak will be discussed in detail in Sec. III B 5. After deposition of 2 DL Si, a Ga $3d$ peak with three components is obtained: bulk, Ga-Si, and Ga-Ga. The As $3d$ peak of the clean GaAs(111)A-(2×2) surface is composed of two doublets. We assign these doublets to bulk and adsorbed As. A surface peak was not observed, so we conclude that all As atoms are in a bulklike environment. The existence of adsorbed As on this Ga-terminated surface can be expected, because this surface was prepared simply by removing the native oxide under As flux. After deposition of 0.5 ML of Si the adsorbed (ads.) component vanished, but a new peak at lower binding energy was detected. The simplest assignment for this new peak is As-Si bonding. However, a simple charge-transfer argument would expect the As-Si bonding component to be at higher binding energy than the bulk As-Ga bonding component. A good explanation for this

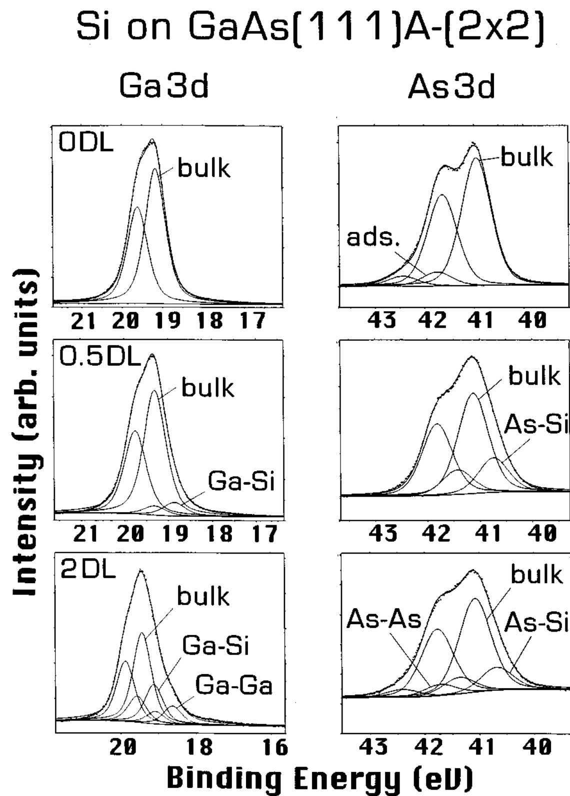

FIG. 4. Surface sensitive Ga 3d and As 3d core-level spectra of GaAs(111)A surfaces as a function of Si overlayer thickness. The Ga 3d spectrum of the uncovered surface contains only the substrate component (bulk). After deposition of Si, Ga-Si bonds are formed. After deposition of 4 ML of Si, Ga-Ga bonds are formed at the interface. Before deposition of Si, adsorbed As produces a spectral component (ads.) at the high binding energy side of the As 3d spectrum. After deposition of Si, As-Si bonds are formed on the surface. After deposition of 4 ML of Si, As-As bonds are also formed. Please note the comment in Ref. 34.

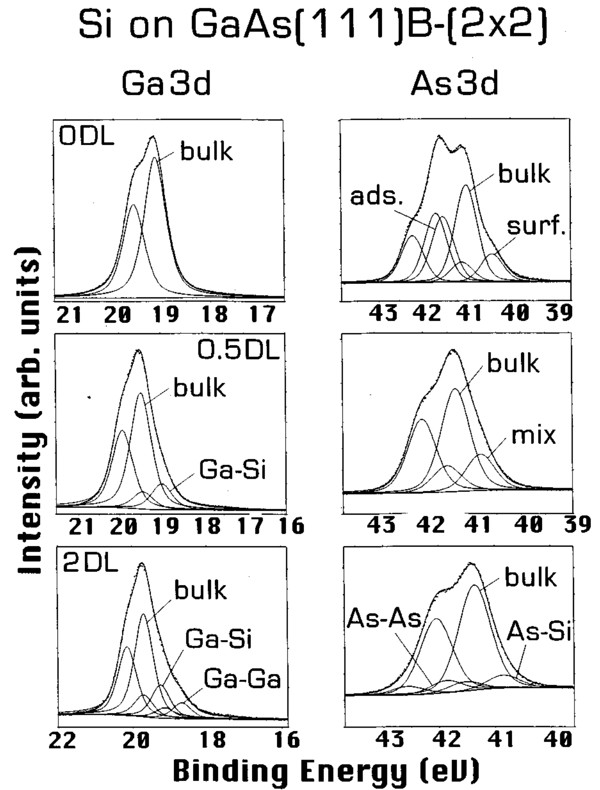

FIG. 5. Surface sensitive Ga 3d and As 3d core-level spectra of GaAs(111)B surfaces as a function of Si overlayer thickness. The Ga 3d spectrum of the uncovered surface contains only the substrate component (bulk). After deposition of Si, Ga-Si bonds are formed. After deposition of 4 ML of Si, Ga-Ga bonds are formed at the interface. As 3d presents a single surface-shifted component (surf.). Before deposition of Si, adsorbed As produces a spectral component (ads.) at the high binding energy side of the spectrum. After deposition of Si, As-Si bonds are formed on the surface. For a coverage of 0.5 ML of Si the surf. and As-Si components coincide as one component (mix). After deposition of 4 ML of Si, As-As bonds are also formed. Please note the comment in Ref. 34.

discrepancy cannot be given at the moment. At least we take comfort from the fact that Bachrach *et al.* found a similar chemical shift.[11] They concluded that the Madelung energy of the surface has to be included in a precise calculation of the shift. After deposition of 2 DL Si on GaAs(111)A-(2×2) we observed a third component in the As 3d peak, which is caused by As-As bonds. The intensity ratio r between the As 3d and the Ga 3d peaks increased from stoichiometric $r=0.6$ for the clean surface to $r=1.9$ after deposition of 2 DL Si. The same ratio, measured by XPS, is constant, so the As enrichment occurs only at the surface.

5. As-rich GaAs(111)B-(2×2)

The spectra measured on the As-rich GaAs(111)B-(2×2) surface are shown in Fig. 5. It is well known that for this surface all Ga atoms are in a bulklike environment, so no surface peak is observed in the Ga 3d core-level spectrum.[25,27] Consequently, this peak can be described very well by a single bulk doublet. The peak shape changes after deposition of 0.5 DL Si. As in the case of Si on GaAs(111)A, a new component appears at the lower binding energy side of the bulk component. This component is assigned to Ga-Si bonds. In contrast to the As-Si bond component, this component is shifted in the expected direction. Since Si is less electronegative than As, the Ga-Si bonding component is at lower binding energy than the Ga-As bulk bonding component. After deposition of 2 DL Si, a third component is found in the Ga 3d core-level spectrum and assigned to Ga-Ga bonds. The As 3d peak of the clean GaAs(111)B-(2×2) surface shows a very strong component of adsorbed excess As and a bulk and a surface component. This deconvolution agrees well with that published by Katnani *et al.*[27] After deposition of 0.5 DL Si at 450 °C the ads. component has completely vanished, and the surface component has slightly changed, so we conclude that As-Si bonds were created. After deposition of 2 DL Si an As-As bond component appears in the As 3d peak, as well as bulk and As-Si bonding components. The intensity ratio r in the As 3d to the Ga 3d peak for the clean surface is $r=0.9$. After subtracting the adsorbed component we obtained stoichiometric $r=0.6$. However, deposition of Si causes a strong segregation of As to the surface. The value of r increased to 1.3 after deposition of 0.5 DL and to $r=2.7$ after deposition of 2 DL of Si.

IV. DISCUSSION

The growth of Si on As-rich GaAs(100) can be described by a simple model: The starting surface, GaAs(100)-(2×4), is As terminated and we observe As-As bonds. The (2×4) structure is known to be built up by As dimers,[32] and these dimers have As-As bonds. Deposition of 0.5 ML Si completely destroys the As-As bonds. The Si bonds to As atoms of the first layer. No Si-Ga bonds were observed in our experiments. The simplest explanation for these findings is the assumption that the Si occupies the equivalent of next-layer Ga sites. This is in agreement with our RHEED results.[15] The deposition of Si on an As-rich GaAs(100)-(2×4) surface leads to the formation of a single-domain (1×2) surface. It can be assumed that the dangling bonds of Si are saturated by the formation of Si dimers, as observed on the clean Si(100) surface.[33] From the orientation of the RHEED pattern we can conclude that the silicon dimers are perpendicular to the As dimers of the reconstructed GaAs substrate, which means that the Si atoms occupy Ga equivalent sites. The same observation was made by Lo´pez *et al.* in their RHEED experiments.[12] During the growth of Si we find no indication for a segregation of As or Ga to the surface. This was also excluded by Bachrach *et al.*[11] who found that the Ga and As $3d$ peaks attenuate with the Si coverage, but that the ratio remains approximately constant. In our experiments we found the Ga $3d$ peak virtually unchanged by the deposition of Si, so we exclude the formation of Ga-Si bonds. However, Chambers and Loebs observed in their experiments the formation of Ga-Si bonds.[22] They measured the Ga $3d$ peak of GaAs(100)-(2×4) before and after deposition of 9 Å Si by XPS Al $K\alpha$ radiation and in normal emission. Since this method is not very surface sensitive, they had some trouble determining the chemical shift of the Ga-Si component. The shift relative to the substrate doublet varied from -0.35 to -0.75 eV. However, the value that we obtained in our experiments, -0.41 eV$\pm$0.06 eV, is within the range they report. Chambers and Loebs deposited the Si with different As-doping concentrations. They found out that the amount of Ga consumed in bonding to Si was somewhat greater when Si was evaporated alone, as opposed to that associated with coevaporation with As. This could indicate that the surface on which they deposited pure Si was not really As terminated but that prior to deposition of Si some As evaporated from the surface, leaving Ga atoms behind at the surface. These Ga atoms could bond to the Si atoms. When Chambers and Loebs deposited the Si under As flux, the number of Ga atoms at the surface was reduced, and so was the number of Ga-Si bonds. Consequently, deposition of Si on a completely As-terminated surface should lead to the formation of As-Si bonds only, as observed in our experiments. In summary, we propose a simple growth model for the epitaxy of Si on As-rich GaAs(100). It is shown in Fig. 6 and explains all features observed in the spectra.

The results obtained after deposition of Si on the Ga-rich surfaces GaAs(100)-$c(8\times2)$ and GaAs(111)A are more complicated, but for these surfaces a consistent growth model can also be offered. The Ga $3d$ and As $3d$ peak components of Ga-rich GaAs(111)A-(2×2) after deposition of 2 DL Si and also the intensity ratio r are very similar to the findings for the Ga-rich GaAs(100)-$c(8\times2)$ surface, so we propose the

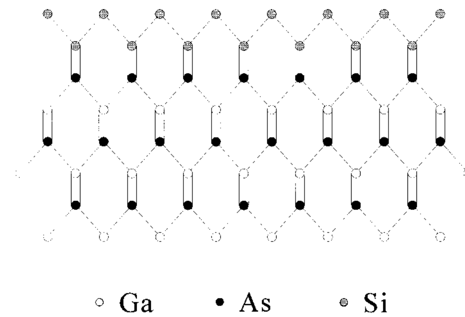

FIG. 6. Proposed growth model for the epitaxy of Si on As-terminated GaAs(100).

same growth model for both surfaces. In the Ga $3d$ peak the formation of Ga-Si and Ga-Ga bonds was observed after deposition of Si. Since these surfaces are Ga rich, we conclude that the Ga-Si bonds are formed at the interface between GaAs and Si. This is further supported by our RHEED experiments.[15] After deposition of Si the GaAs(100)-$c(8\times2)$ reconstruction was converted into a single-domain (2×1) reconstruction. Following the same argument as for GaAs(100)-(2×4) we again conclude that Si dimers are formed, but on this surface perpendicular to the Ga dimers of the $c(8\times2)$. This means that the Si atoms occupy As equivalent sites. According to Le Lay *et al.*, the GaAs(100)-$c(8\times2)$ or (4×2) reconstructions are explained by a missing Ga dimer row model.[20] There are inequivalent dimers in the cell: one type-1 dimer surrounded by two type-2 dimers next to the missing dimer row. Le Lay *et al.* assign the $S1$ component to Ga in type-1 dimers and the $S2$ component to Ga in type-2 dimers. After deposition of 0.5 ML Si we found the $S1$ component unchanged with respect to the bulk component. This could indicate that the first Si atoms nucleated in the missing dimer row and consequently did not affect the type-1 dimers. This would also explain the occurrence of both Ga-Si and As-Si bonds after deposition of 0.5 ML Si. The situation is more complicated after deposition of 4 ML Si. From the peak intensity ratio we conclude that As has segregated to the surface. A condensation of As atoms on the surface from the gas phase can be excluded, because it did not occur on the As-rich GaAs(100) surface under the same experimental conditions. Also bulk diffusion of As can be excluded at the temperatures used here.[13] Probably a surface exchange reaction of As atoms with the arriving Si adatoms takes place. A similar rise in the As/Ga intensity ratio with Si coverage was observed by Bachrach *et al.* on the Ga-rich GaAs(100)-(4×6) surface.[11] Since we observe As-As bonds as well as As-Si bonds, the amount of As on the surface is probably larger than 1 ML. The As segregates from the GaAs substrate to the surface of the Si film, and it leaves As vacancies behind at the interface. These vacancies can be filled by Si atoms, or Ga atoms can move to antisites, causing the observed Ga-Ga bonds. Zalm, Marée, and Olthof[13] report a surplus of Ga on the surface of Si layers deposited on GaAs(100)-$c(8\times2)$ as measured by Auger electron spectroscopy (AES). This is clearly refuted by our results and also conflicts with the results of Bachrach *et al.*[11] In another AES work, Gonzáles, Soria, and Alonso report the segrega-

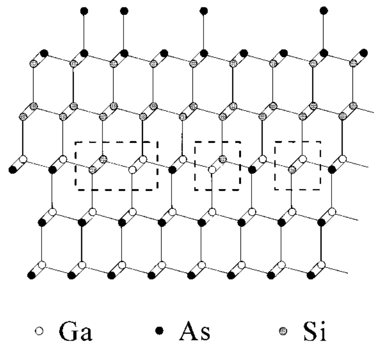

FIG. 7. Proposed growth model for the epitaxy of Si on GaAs(111)A. Three different kinds of interface defects are shown. In the left box Ga is on an antisite, forming a Ga-Ga bond. The remaining vacancies are filled by two Si atoms. Also in the middle box Ga is on an antisite. In the right box, an As vacancy is filled by a Si atom.

tion of both As and Ga atoms to the top Si layer[14] when deposited on GaAs(111)A. From our data we cannot exclude the segregation of Ga to the surface, but we observe a clear increase in the As-Ga ratio at the surface. This means that the number of As atoms at the surface must be clearly larger than the number of Ga atoms. Consequently, in our simple model of the growth of Si on Ga-rich GaAs surfaces we neglect any Ga segregation to the surface. In summary, we propose a growth model for the epitaxy of Si on GaAs(111)A. It is shown in Fig. 7 and explains all features observed in the spectra. The position of the As atoms at the surface is consistent with models for As-terminated Si(111).[28,29] These models seem applicable to this structure, because in both cases a (1×1) RHEED pattern is observed.[15,28] Three kinds of interfacial defects are sketched in the figure. An As vacancy can be filled by a Si atom, producing a Ga-Si bond. This is shown in the rightmost box in Fig. 7. Secondly, an As vacancy can be filled by a neighboring Ga atom. The created Ga vacancy is then filled by a Si atom. This situation is sketched in the middle box of Fig. 7. If As vacancies are formed on two neighboring GaAs sites, one of the two remaining Ga atoms can move to an antisite and form a Ga-Ga bond. The remaining vacancies are filled by Si atoms. This situation is sketched in the leftmost box in Fig. 7.

The situation is even more complicated for the Si epitaxy on the As-rich GaAs(111)B surface. The experimental results are unequivocal. The features obtained in the spectra are the same as for the Ga-rich surfaces. But while Ga-Si bonds can be expected on a Ga-rich surface, the formation of Ga-Si bonds is difficult to explain on an As-rich surface. However, no similarity between the As-rich GaAs(100) and (111) surfaces was found in our experiments. Unfortunately, there is little information in the literature about this system to compare our results against. Gonzáles, Soria, and Alonso made AES measurements on the GaAs(111)B surface. They observed a surface segregation of Ga and As atoms during the growth of Si. In addition, for this surface they give diffusion coefficients for As and Ga in Si for different temperatures. In general, the diffusion coefficient D_{As} for As is larger than that for Ga, D_{Ga}. According to their data, D_{As} at 450 °C is approximately three times larger than D_{Ga}. This could explain the As enrichment at the surface observed in our experiments. A model for the surface unit cell of the GaAs(111)B-(2×2) reconstruction is proposed in Ref. 30. The surface consists of first-layer As atoms and second-layer Ga atoms. On top of the first As layer, As trimers are formed, which are arranged in a (2×2) periodicity. From our RHEED experiments we conclude that the As trimers are destroyed during the very early stage of Si deposition. After deposition of 0.5 DL of Si the (2×2) superstructure had already disappeared and a (1×1) surface was observed. However, this (1×1) periodicity is given by the first-layer As atoms. One would expect bonding between these As atoms and the deposited Si atoms. However, instead Ga-Si bonds are formed. This means that some of the first-layer As atoms must be replaced by Si atoms. But a simple replacement seems very unlikely because it requires an energy of 2.49 eV per replacement.[31] Furthermore, it was not observed on the As-rich GaAs(100) surface. While the surface As atoms of the GaAs(100)-(2×4) have two bonds with the second-layer Ga atoms, there are three bonds for the GaAs(111)B surface. Consequently, the As should be even harder to replace on the GaAs(111)B surface. Anyway, if we assume a replacement of As atoms by Si atoms, then we have nearly the same situation as on the GaAs(111)A surface, and we can expect a similar growth mode. However, the main obstacle still remains: In which way are the Ga-Si bonds formed? More detailed studies are probably necessary to clarify this point.

Another interesting question is as follows: Why do we observe an As segregation for almost all substrates except the As-rich GaAs(100) surface? The answer could be the stability of this surface. Very stable As dimers are known to be formed on the GaAs(100)-(2×4) surface. During deposition of Si no simple exchange reaction can take place, because all As atoms are bound in dimers. Probably immediately after Si has broken an As dimer, As-Si bonds and later Si-Si dimers are formed. These Si dimers could act as a very strong diffusion barrier for As atoms.

V. CONCLUDING REMARKS

The epitaxy of Si on the different surfaces of GaAs is so far not completely understood. The variety of possible reactions at the interface and at the surface does not allow a precise determination of the processes with just structural methods like RHEED. In addition, the chemical bondings at the interface and at the surface have to be investigated. In this paper we employ very surface sensitive synchrotron radiation photoelectron spectroscopy to clarify the chemical bondings at interface and surface in great detail.

Good epitaxial quality of Si on all the GaAs substrates under investigation was proved by RHEED. A thin Si layer can be used in all cases for surface passivation. The strong band bending due to the Fermi-level pinning in the midgap of the GaAs substrates is relaxed. On the As-rich GaAs(100) surface the Si grows without the creation of interfacial defects. Furthermore, we find no indication for a surface segregation of As or Ga. This makes Si a very promising material for an interface control layer on GaAs.

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